REMARKS

Claims 90, 92, 93, 95-98, 100-103, 105-111, 113-115 and 144-147 are all the claims pending in the application. By this Amendment, Applicant adds claim 148, which is clearly supported throughout the specification.

I. Summary of the Office Action

The Examiner rejected all pending claims under 35 U.S.C. § 103(a). In addition, claims 90, 92, 93, 95-98, 100-103, 105-111, 113-115, and 144-147 are rejected on the ground of nonstatutory obviousness-type double patenting.

II. Claim Rejection under 35 U.S.C. § 103

Claims 90, 92, 93, and 95-98 are rejected under 35 U.S.C. 103(a) as being unpatentable over Saito (Japanese Patent Application Publication Number 05-148615, hereafter Saito, using the machine translation thereof) in view of Imai et al. (Japanese Patent Application Publication Number 11-229159, hereafter Imai, using the machine translation thereof). Claims 100, 103, 105-108, 110, 111, 113-115, and 144-147 are rejected under 35 U.S.C. 103(a) as being unpatentable over Saito. Claims 101 and 109 are rejected under 35 U.S.C. 103(a) as being unpatentable over Saito in view of Imai (Japanese Patent Application Publication Number 11-229159, hereafter Imai, using the machine translation thereof) and further in view of Koizumi et al (EP 1035231, hereafter referred to as Koizumi). Claims 102, 110, and 144-147 are alternately rejected under 35 U.S.C. 103(a) as being unpatentable over Saito, as applied to claim 100, in view of Koizumi II (US 6336950) in view of Pratt (US 5818005). Applicant respectfully traverses these grounds of rejections at least in view of the following exemplary comments.

Of these rejected claims, claims 90, 95, 100, and 108 are independent. Independent claims 90, 95, 100, and 108 recite: "the powder of any of the metal and the metallic compound is any one of Co alloy, Ni alloy, and Fe alloy." Applicant respectfully submits that the prior art of record do not disclose or suggest at least these unique features of the independent claims.

The Examiner alleges that Saito in ¶¶ 16-19 describe the powder to be a Co alloy, Ni alloy, and/or Fe alloy (*see* page 3 of the Office Action). Applicant respectfully disagrees.

To further Examiner's understanding, Applicant respectfully submits a complete English translation of the Saito reference herewith. As noted in Saito, various types of metallic materials or non-metallic materials are possible as the coating material, with examples including metal **or** alloy, nonmetallic elements, ceramics, carbides, nitrides, borides, etc. Specifically, in terms of hard materials, carbides such as WC, TiC, TaC, ZrC and SiC, borides such as TiB_2 and ZrB_2, nitrides such as TiN and ZrN (fine ceramics) can be used for coating alone or with added sintering aid. Furthermore, metallic materials such as W and Mo and corrosion-resistant materials such as Al, Ti, Ni, Cr and Co can also be used. In addition, diamond, Al_2O_3, Si_3N_4 and the like, which have no electrical conductivity, may be used for coating mixed with electrically conductive materials such as iron powder, cobalt powder, nickel powder, chromium powder, copper powder, etc. Essentially, the material may be selected in connection with the surface characteristics to be imparted (¶ 16).

Saito, however, does not disclose or suggest the powder or powder compound being a Co alloy, Ni alloy, and/or Ni alloy. Saito describes adding a conductive additive to a non-conductive cover material. Among the additives mentioned are elemental iron, cobalt, chromium

or copper, in powder form. Saito does not disclose or suggest the powder being an alloy *i.e.*, Co alloy, Ni alloy, and/or Fe alloy. Moreover, in Saito, the added powder is an additive and not a main component of the electrode.

Imai, Koizumi, Koizumi II, and Pratt do not cure the above-identified deficiencies of Saito.

Accordingly, Applicant respectfully submits that claims 90, 95, 100, and 108 should now be allowed. Claims 92, 93, 96-98, 101-103, 105-107, 109-111, 113-115, and 144-147 are patentable at least by virtue of their dependency.

In addition, dependent claim 103 recites: "the small-diameter particle and the large-diameter particle have an identical component." The Examiner now alleges that Saito teaches selecting appropriate materials to produce desired film and such selection is within the level of one of ordinary skill in the art (*see* pages 21-22). Applicant respectfully disagrees.

Applicant respectfully notes that although Saito describes mixing various different materials, there is no disclosure or even remote suggestion of mixing the same material that has different particle diameter. That is, Saito (as well as Imai) fails to recognize the importance of mixing a material of different diameters for improved density of the electrode. Accordingly, although Saito may describe using different materials, it clearly does not and would not describe using the same material of different diameters. In fact, the above-quoted features of claim 103 are unique features of the claim *e.g.*, pages 49-53 of the specification and are not an obvious variation. For at least these additional exemplary reasons, claim 103 is patentable over Saito.

III. Claim Rejection for Double Patenting

A. Claims 90, 92, and 95-98 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-7 of U.S. Patent No. 7,641,945 (hereafter referred to as '945).

B. Claims 100, 102, 103, 105-108, 110, 111, 113-115, and 144-147 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-7 of U.S. Patent 7,641,945 in view of Saito.

C. Claims 101 and 109 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 1-7 of U.S. Patent 7,641,945 in view of Koizumi.

D. Claims 100, 102, 103, 105, 106, 108, 110, 111, 113, 114, and 144-147 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 76-78, 105 and 106 of copending Application No. 10/559,427 (hereinafter referred to as '427) in view of Saito.

E. Claims 90, 92, 93, and 95-98 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 76-78, 105 and 106 of copending Application No. 10/559,427 in view of Saito further in view of Imai.

F. Claims 101 and 109 are provisionally rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 76-78, 105 and 106 of copending Application No. 10/559427 in view of Saito and Koizumi.

G. Claims 100, 102, 103, 105, 106, 108, 110, 111, 113, 114, and 144-147 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 46, 51 and 52 of U.S. Patent No. 7,537,808 (which was previously used in the provisional double patenting rejection before it issued as Application 10/516,506) in view of Saito.

H. Claims 90, 92, 93, and 95-98 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 46, 51 and 52 of U.S. Patent No. 7,537,808 in view of Saito and Imai.

I. Claims 101 and 109 are rejected on the ground of nonstatutory obviousness-type double patenting as being unpatentable over claims 46, 51 and 52 of U.S. Patent No. 7,537,808 in view of Saito in view of Koizumi.

Applicant respectfully submits that as argued above with respect to the prior art rejections, Saito, Imai, and Koizumi do not describe the above-quoted unique features of at least amended claims 90, 95, 100, and 108. As such, these references do not cure the deficiencies of the '945 patent, the '427 application, and the '808 patent. Accordingly, Applicant respectfully requests the Examiner to withdraw these double patenting rejections.

IV. New Claims

In order to provide more varied protection, Applicant adds claim 148, which is patentable by virtue of its dependency and for additional features set forth therein.

V. Conclusion

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly invited to contact the undersigned attorney at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

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(54) (TITLE OF THE INVENTION) Surface treatment method for metallic materials

(57) (ABSTRACT)

(PURPOSE) To inexpensively form a strong coating layer having adequate thickness and the desired surface characteristics, such as corrosion resistance and heat resistance, without the disadvantages of dimensional change and reduction in hardness (strength) of the base material due to holding of the entire metallic material of the base material at a high temperature, or peeling of film, etc.

(CONSTITUTION) The surface of a base material consisting of metallic material is coated with a metallic or non-metallic material, after which the built-up material is remelted a small area at a time by means of pulse electric discharge machining in a liquid, gas or vacuum, causing the base material and the coating material to diffuse and blend, thereby forming a compact coating layer on the base material surface. Metal or alloy, non-metallic elements, ceramics, carbides, nitrides, borides, etc. can be used as the coating material. Thermal spraying, electrodeposition, low temperature vapor deposition, electric discharge deposition employing consumable electrodes, etc. can be used as the means of coating with the coating materials. Pulse electric discharge machining is preferably performed using a non-consumable electrode as the negative pole. It is also possible to perform coating with the coating material and pulse electric discharge machining one layer at a time and provide the coating layers with graded characteristics so as to produce a so-called functionally graded material.

(SCOPE OF PATENT CLAIMS)

(CLAIM 1) A surface treatment method for metallic materials, characterized in that the surface of a base material comprising metallic material is coated with metallic or non-metallic material, after which the built-up material is remelted a small area at a time by means of pulse electric discharge machining in a liquid, gas or vacuum, causing the base material and the coating material to diffuse, blend, and form a compact coating layer on the base material surface.

(CLAIM 2) The method described in Claim 1, wherein the coating material is one or two or more from among metals or alloys, non-metallic elements, ceramics, carbides, nitrides and borides.

(CLAIM 3) The method described in Claim 1, wherein the coating means for the coating material is any one from among thermal spraying, electrodeposition, low temperature vapor deposition or electric discharge deposition using consumable electrodes.

(CLAIM 4) The method described in Claim 1, wherein pulse electric discharge machining is performed using a non-consumable electrode as the negative electrode.

(CLAIM 5) The method described in Claim 1, wherein coating with coating material and pulse electric discharge machining are performed one layer at a time and graded characteristics are imparted to the coating layer.

(DETAILED DESCRIPTION OF THE INVENTION)

(0001) The present invention relates to surface treatment technology for metallic materials; more specifically, the invention relates to a surface treatment method which forms a compact layer having the desired characteristics, such as heat resistance, corrosion resistance, wear resistance, hardness, etc., on the surface, without the problems of dimensional change or thermal hysteresis of the base material.

(0002)

(PRIOR ART AND PROBLEMS TO BE SOLVED BY THE INVENTION) CVD (chemical vapor deposition), PVD (vacuum deposition), electrodeposition, nitriding, electrochemical plating, electroless plating and the like are known in the prior art as means of imparting wear resistance, corrosion resistance and the like to a metal surface.

(0003) However, CVD and PVD involve coating by raising the temperature of the base material to at least 360°C and up to about 1100°C, and are widely known to consequently have the disadvantage of causing dimensional changes or reduction in hardness of the base material. The hardened layer is thin, at several μm. Furthermore, nitriding has the difficulty of processing steel by heating to about 500°C.

(0004) In a surface created by electrodeposition, the deposited metal is merely built up or deposited on the base material and is not diffused, and is well known to peel off easily, and there are also the disadvantages of causing hydrogen embrittlement, etc. The same is true of electrochemical plating and electroless plating.

(0005) It is already known that coatings built up on a base material surface by thermal spraying are porous and peel off easily. Furthermore, even if one remelts with laser light, the heat input will be nonuniform depending of the location of the spot, and streaking will occur at the boundaries of beam advancement, so it is not possible to obtain an esthetically pleasing surface. Furthermore, with laser light or the like, application to three-dimensional machined shapes, as shown in Figure 1, is structurally problematic.

(0006) Moreover, with conventional surface treatment methods, diffusion hardly occurs, so it is difficult to coat to an adequate thickness (e.g. several tens of μm to 100 μm) with materials that do not diffuse readily, such as fine ceramics.

(0007) The object of the present invention is to resolve the aforementioned problems of the prior art and provide a surface treatment method which makes it possible to form a strong coating layer having adequate thickness and the desired surface characteristics, such as corrosion resistance and heat resistance, without the disadvantages of dimensional change and reduction in hardness (strength) of the base material due to holding of the entire metallic material of the base material at a high temperature, or peeling of film, etc.

(0008)

(MEANS FOR SOLVING THE PROBLEM) To resolve the aforementioned problems, the present inventors first made concerted research efforts on surface treatment methods which do not require exposing the entire metal material to high temperatures. As a result, the finding was obtained that a strong coating layer can be formed without causing deformation or reduction in hardness of the base material if the coating material can be built up in advance on the surface of the metallic material by a method that does not heat the base material to a high temperature, and if the built-up material can be remelted microscopically, i.e. in small areas, so as to cause diffusion and blending into the base material.

(0009) Upon further researching approaches that would allow such microscopic remelting of the built-up material, the inventors discovered that this is possible by applying pulse electric discharge machining. Electric discharge machining is a machining method generally well known as a machining method for removal machining of shapes utilizing electric discharge phenomena, but the present inventors developed a completely novel usage involving the microscopic remelting of built-up material by means of electric discharge energy.

(0010) Namely, the gist of the present invention is a surface treatment method for metallic materials, characterized in that the surface of a base material comprising metallic material is coated with metallic or non-metallic material, after which the built-up material is remelted a small area at a time by means of pulse electric discharge machining in a liquid, gas or vacuum, causing the base material and the coating material to diffuse, blend, and form a compact coating layer on the base material surface.

(0011) The present invention will be described in greater detail below.

(0012)

(OPERATION)

(0013) As stated above, the adhesion, deposition and buildup of coating materials by thermal spraying, electrodeposition, vapor deposition and electric discharge deposition on the surface of metallic materials is known. It should be noted that the method of electric discharge deposition is a surface treatment method previously proposed by the present inventors ("Proceedings of the Technical Symposium of the 1991 Annual Spring Meeting of the Japan Society for Precision Engineering" (March 26, 1991), p. 463), whereby an electrically conductive material to be deposited is molded into a green compact and is used as an electrode in electric discharge machining, with which machining is performed to deposit the green compact material on the other metal. However, this built-up material does not diffuse into the base material and thus has weak adhesive strength.

(0014) The present invention consists in applying pulse electric discharge to such built-up material by the technique of electric discharge machining in liquid, gas or vacuum, thereby generating a high temperature locally (at the electric discharge point) and thus remelting and diffusing the built-up material into the base material essentially without the raising the mean temperature of the base material.

(0015) In the present invention, the means of coating the surface of the metallic material with the coating material is not particularly restricted, but methods which do not expose the base material to high temperatures are recommended. Examples include, but of course are not limited to, the aforementioned thermal spraying, electrodeposition, low temperature vapor deposition, electric discharge deposition using consumable electrodes, etc. From the standpoint of the relationship to pulse electric discharge machining, which is carried out as a subsequent process, electric discharge deposition is preferable.

(0016) Various types of metallic materials or non-metallic materials are possible as the coating material, with examples including metal or alloy, nonmetallic elements, ceramics, carbides, nitrides, borides, etc. Specifically, in terms of hard materials, carbides such as WC, TiC, TaC, ZrC and SiC, borides such as TiB_2 and ZrB_2, nitrides such as TiN and ZrN (fine ceramics) can be used for coating alone or with added sintering aid. Furthermore, metallic materials such as W and Mo and corrosion-resistant materials such as Al, Ti, Ni, Cr and Co can also be used. In addition, diamond, Al_2O_3, Si_3N_4 and the like, which have no electrical conductivity, may be used for coating mixed with electrically conductive materials such as iron powder, cobalt powder, nickel powder, chromium powder, copper powder, etc. Essentially, the material may be selected in connection with the surface characteristics to be imparted.

(0017) After the surface of the metallic material has been coated with the coating material, pulse electric discharge machining is applied microscopically or a small area at a time to remelt the built-up material and cause it to disperse and blend into the base material. The pulse electric discharge machining can be conducted in liquid, gas or vacuum, and involves generating an electric discharge between the built-up material as one electrode, and another electrode.

(0018) For pulse electric discharge machining, it is desirable to use a non-consumable electrode, or an electrode of a composition close to that of built-up material. For example, if WC is mainly built up on the metallic material surface, a material comprising sintered WC-Co (e.g. tool tip material) would be used as the electrode.

(0019) Electric discharge is generated at about several hundred times to several tens of thousands of times per second. The machined surface is a surface of accumulated small microscopic electric discharge marks. High temperature and pressure are generated for a short time of 10 μs to 1000 μs in a small area but at a high electric discharge mark current density of several tens of thousands of A/cm^2. The surface temperature of an electric discharge point is at around the boiling point of the material, and the pressure at that point is several thousands of kgf/cm^2, so while a portion of the melted material is dispersed, the remaining part remelts and diffuses into the base material. Since the electric discharge time is short, the electric discharge point is immediately cooled and the mean temperature of the base material does not rise.

(0020) Preferable parameters for pulse electric discharge machining are power supply voltage: 60 to 100 V, pulse discharge current (Ip): 1 to 100 A, pulse width (τp): 5 to 2000 μs, rest time (τr): 5 to 2000 μs. Generally, when Ip is low, τp would be made shorter, and if Ip is high, τp would be made longer, so that for instance, if the pulse discharge current Ip is low, for example, at Ip = 3 A, τp would be 16 μs, and if Ip is high, for instance, Ip = 50 A, then τp would be 2000.

(0021) With the surface treatment method of the present invention, a dense layer having the desired characteristics, such as heat resistance, corrosion resistance, wear resistance and hardness, can be formed on the surface of metallic materials, such as inexpensive carbon steel or other ferrous materials. Even with materials that do not readily diffuse into steel, such as fine ceramics, through remelting, it is possible to obtain strong adhesion and diffusion into the base material. Furthermore, with materials such Al, Ti, Ni, Cr and Co, which readily dissolve in ferrous materials, stronger surface treatment becomes possible by performing pulse electric discharge treatment. Namely, when high speed electric discharge is performed using high current to increase the speed of electric discharge deposition, even with materials such as Al, Ti, Ni, Cr and Co, which readily dissolve in ferrous materials, diffusion into the base material will be inadequate and the deposited condition will be highly irregular, but when pulse electric discharge treatment is used, diffusion is promoted through remelting. Furthermore, in the case of electrodeposition or electroplating, when the plating speed is increased at a high current density, only a rough plating layer of low adhesion will be obtained, but when pulse electric discharge machining is performed, a surface layer of high adhesion can be formed. When pulse electric discharge treatment is performed on a coating of nonconductive hard material such a diamond, Al_2O_3 or Si_3N_4 mixed with a conductive metal such as iron powder, cobalt powder, nickel powder, chromium powder or copper powder, the conductive metal will remelt and the nonconductive hard material will strongly adhere to the surface of the base material.

(0022) Furthermore, it is possible to fabricate materials with graded characteristics. A graded material is for example a base material comprising metallic material, in which the content ratio of fine ceramics is gradually increased outward from the base material side, with a markedly higher content ratio of fine ceramics at the surface of the material. Compared to a material in which metallic material and fine ceramics are merely joined or coated, this sort of graded material has less shear stress and bending stress occurring at the joint surface due to marked differences in coefficients of expansion in case of temperature rise, and is thus not prone to rupture, etc. while being used at high temperatures. This is because even if thermal expansion should occur due to temperature rise, the stress will be moderated.

(0023) Next, examples of embodiment of the present invention will be presented.

(0024)

(Example of Embodiment 1) Al powder was compressed and used as one electrode, and an Fe-Al alloy layer was obtained on the surface of a base material (S50C, quenched and tempered material) by electric discharge deposition as shown in Figure 1. The reason for using an Al green compact is that if Al is used as a powder, the apparent thermal conductivity drops to 1/2–1/3; furthermore, the strength of the electrode material becomes weaker, so buildup on the base metal through electric discharge is easier. The electric discharge machining parameters are shown in

(Table 1)

Item	Electric discharge deposition machining parameters using Al green compact
Electrode	Al green compact, molding pressure: 4 tons, other: see table 3
Work piece	S50C (quenched and tempered material)
Machining liquid	Diamond EDF
Electrode polarity	(–)
Machining parameters	Ip: 10 A, τp: 256 μs, τr: 256 μs
Machining time	5 min

(0025) EPMA analysis results for the obtained alloy layer are shown in Figure 2, and X-ray diffraction analysis results are shown in Figure 3. Based on Figure 2, Al of the electrode material is present on the machined surface at a thickness of 30 μm with graded characteristics (more on the surface, less inside). From Figure 3, a very strong $AlFe_3C_{0.5}$ peak can be observed. This compound is known as an intermetallic compound with excellent oxidation resistance. In this way, with Al, there are cases where adequate surface treatment is possible with electric discharge deposition.
(0026) However, with fine ceramics (WC, TiC, TaC, ZrC, SiC, TiB_2, ZrB_2, TiN, ZrN, etc.) and high melting point materials such as W and Mo, it is often difficult to achieve adequate diffusion inside the base material through electric discharge deposition alone. Thus, in the present example, the case will be presented where, from among those materials, WC is deposited by electric discharge and then pulse electric discharge machining is applied thereto.
(0027) First, WC powder (mean particle diameter 3 μm) was mixed with Fe powder (mean particle diameter 9.8 μm) at the ratio of 1:1, and compression molding (compression pressure 4 t/cm^2) was performed to create a green compact. This was adhered with electrically conductive adhesive to a round copper rod to create an electrode. Next, using carbon steel (S55C untreated material) as the base material, the machining parameters (Ip, τp, τr) were modified and an electric discharge machining experiment was performed as shown in Figure 1.
(0028) As a result, under machining conditions with a relatively large D.F. (duty factor), the arc generated by electric discharge was focused and the electrode was destroyed, but under conditions with a D.F. of 1.5% or less, the WC electrode was stably consumed without collapsing, and adhered to the base material surface. The machining parameters here were Ip = 20A, τp = 16 μs, τr = 1024 μs.
(0029) The results of performing X-ray diffraction on the specimen surface after machining showed a WC peak, as shown in Figure 4. The results of measuring the adhered quantity of WC (the height from the base material surface) based on machining time using the focal depth method, as shown in
(Table 2)

Machining height \ Machining time	20 minutes	30 minutes	50 minutes	90 minutes
Central area (μm)	6.6	11.1	19.6	51.9
Edge area (μm)	5.5	27.1	80.7	65.4

were that making the machining time longer increases the amount of adhesion of WC to the base material surface. WC adhering to the base material surface had weak adhesion and could be peeled off with a screwdriver or the like.
(0030) Next, the material obtained by the aforementioned electric discharge machining was subjected to pulse electric discharge machining as outlined below.
(0031) First, a WC-Co sintered compact was adhered to a round copper rod with electrically conductive adhesive to fashion an electrode (finishing electrode). Next, using this finishing electrode, pulse electric discharge machining was performed starting from the top of the WC and Fe built-up layer adhering to the base material surface. Regarding the machining parameters, machining was performed with the circuit configuration shown in Figure 5, setting the electrode polarity to negative and changing Ip, τp and τr so as not to excessively machine the base material. The pulse waveform (square wave) is shown in Figure 6. The results of X-ray diffraction performed on the surface after machining are shown in Figure 7, and the analysis results are presented in
(Table 3)

Ip / τp(τr)	20	10	3
16 (1024)	×	O	O
64 (256)	O	O	O
1024 (1024)	O	O	O

(Note) ×: WC not detected
O: WC detected

As shown in the same table, with a short pulse width (τp), high current (Ip) and long machining time, the built-up material disappears, but under conditions where τp is somewhat long and current (Ip) is somewhat low, dispersion of the built-up WF-Fe material can be reduced, and WC is detected.

(0032) With electric discharge deposition, as shown in Figure 8 (cross-sectional micrograph), the adhesion of WC-Fe is weak, but when pulse electric discharge machining was performed thereon, it was confirmed that WC diffuses into the base material, as shown in Figure 9 (cross-sectional micrograph) and Figure 10 (cross-sectional SEM photograph).

(0033) Furthermore, the relationship between distance from the surface and Vickers hardness (Hc [*sic*]) is shown in Figure 11. The hardness of normal WC-Co alloy is about Hv 800 to 1400, and in this experiment, the same level of hardness of the surface treatment layer (Hv 1000 to 1400) was confirmed (the quenched hardness of S55C is over Hv 800). Furthermore, in this experiment, the thickness for which Hv 1000 or greater was obtained was about 60 μm, so the thickness was substantial.

(0034)

(Example of Embodiment 2) Steel (special tool steel) was used as the base material, and a powder electrode comprising a mixture of TiB_2 as the fine ceramic and Fe powder as an aid was employed. First, lamination was performed by electric discharge deposition using the powder electrode, as shown in Figure 12. After lamination, pulse electric discharge machining was performed. Here, the operation was performed in one of two ways: performing lamination and pulse electric discharge machining one layer at a time, and performing pulse electric discharge machining after completing all the laminations.

(0035) As a result, a graded material with coating layers having TiB_2 content that gradually decreases from the surface was obtained. Furthermore, while the former method was time-consuming, the adhesion, etc. was strong. It should be noted that the Vickers hardness of the surface portion was Hv = 2000 to 2500, and the Vickers hardness of areas near the base material was Hv = 550 to 600.

(0036)

(Example of Embodiment 3) Steel (special tool steel) was used as the base material, and a powder electrode comprising a mixture of cobalt powder and diamond powder as the hard material was employed. First, lamination was performed by electric discharge deposition using the powder electrode, as shown in Figure 13. After lamination, pulse electric discharge machining was performed. Here, the operation was performed in one of two ways: performing lamination and pulse electric discharge machining one layer at a time, and performing pulse electric discharge machining after completing all the laminations.

(0037) As a result, a graded material with coating layers having diamond content that gradually decreases from the surface was obtained. It should be noted that the Vickers hardness of the surface portion (areas with more diamond) was Hv = 3500 to 4000, and the Vickers hardness of areas near the base material was Hv = 550 to 600.

(0038)

(Example of Embodiment 4) Machining was performed as shown in Figure 1 to form a dense coating layer of fine ceramics or WC-Co, etc. on the inner surface of the form. First, as shown in Figure 1, three-dimensional shape machining was performed using material conventionally used for electrodes in low consumption electric discharge machining, such as copper or graphite. Then, thermal spraying with TiB_2 powder mixed with about 20% cobalt powder was performed on the inner surface of the machined item. The thickness of the thermal spraying was about 100 μm. The thermally sprayed film was deposited somewhat irregularly, as shown in Figure 14.

(0039) Then pulse electric discharge machining was again performed using an electric discharge machining apparatus with the electrode shown in Figure 1 (either the one used previously, or one with corrected shape and dimensions, or a slightly smaller electrode may be used). The parameters for this machining were Ip = 3 A, τp = 64 μs, τr = 256 μs, electric discharge voltage = approx. 100 V. On the surface of the work piece, a cavity coated with high shape precision was obtained, as shown in Figure 15. This machining makes it possible to fabricate die cast molds for performing high temperature pouring.

(0040) Here, if pulse electric discharge finishing is to be performed using a somewhat small electrode, it would be performed in the same manner as in oscillating machining (a method in which the electrode is moved excentrically in the horizontal direction to machine an area larger than the electrode dimensions by the dimensions of the eccentricity, which increases the finish surface roughness of side surfaces and bottom surfaces), which is well known in electric discharge machining.

(0041) With the method of the present embodiment, cavity shapes which are difficult to machine by the usual machining methods are subjected to electric discharge machining in advance, materials such as fine ceramics are deposited on the inner surface thereof by thermal spraying, etc., and the top thereof is remelted by means of pulse electric discharge machining. Melting by other means such as other lasers or high frequency heating is impossible or difficult here, so this is a very big advantage of the present invention.

(0042) It should be noted that while electric discharge deposition or thermal spraying was used as the means of coating with the coating

material in the above-described examples of embodiment, it is also possible to employ other means such as electrodeposition, low temperature vapor deposition, etc., and of course it is also possible to employ a combination of various coating means.

(0043)

(EFFECT OF THE INVENTION) According to the present invention, as described in detail above, a compact strong coating layer having adequate thickness and the desired surface characteristics, such as corrosion resistance and heat resistance, can be easily formed without disadvantages such as dimensional change and reduction in hardness (strength) of the base material, or peeling of film, etc. For example, the invention can be employed for coating the parts of high temperature turbine blades that are bombarded by high temperature gases or steam, die cavity areas into which high temperature molten metal is cast, shot blasting nozzle parts for molten metal casting dies, and other parts (e.g. injection molding machine pipe parts, etc.), or for coating only the blade parts of steel dies, with fine ceramics.

(0044) Furthermore, functionally graded materials having a so-called functionally graded film in which the composition changes gradually from the top of the base material toward the surface can be manufactured inexpensively.

(BRIEF DESCRIPTION OF THE DRAWINGS)

(FIGURE 1) A drawing intended to explain the main points of electric discharge deposition using a green compact electrode.

(FIGURE 2) A drawing illustrating the results of EPMA analysis of an Al coating layer obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 3) A drawing illustrating the results of X-ray diffraction analysis of an Al coating layer obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 4) A drawing illustrating the results of X-ray diffraction analysis of a WC-Fe coating layer obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 5) A drawing intended to explain the circuit configuration for pulse electric discharge machining.

(FIGURE 6) A drawing illustrating the pulse waveform for pulse electric discharge machining.

(FIGURE 7) A drawing illustrating the results of X-ray diffraction of a WC-Fe coating layer obtained by performing pulse electric discharge machining (finishing) on the WC-Fe coating layer in Example of Embodiment 1.

(FIGURE 8) A cross-sectional micrograph of a specimen (metal structure) obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 9) A micrograph of a cross-section (metal structure) of a specimen obtained by performing pulse electric discharge machining (finishing) on the WC-Fe coating layer obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 10) An SEM photograph of the cross-section (metal structure) of a sample obtained by performing pulse electric discharge machining (finishing) on the WC-Fe coating layer obtained by electric discharge deposition in Example of Embodiment 1.

(FIGURE 11) A drawing illustrating the Vickers hardness (Hv) distribution from the surface of a specimen cross-section obtained by performing pulse electric discharge machining (finishing) on the WC-Fe coating layer obtained by electric discharge deposition in Example of Embodiment 1.

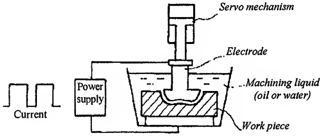
(FIGURE 12) A drawing intended to explain the main points of lamination of coating material in Example of Embodiment 2.

(FIGURE 13) A drawing intended to explain the main points of lamination of coating material in Example of Embodiment 3.

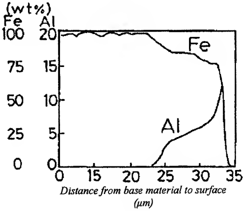
(FIGURE 14) A drawing illustrating the cavity shape obtained by electric discharge machining and thermal spraying in Example of Embodiment 4.

(FIGURE 15) A drawing illustrating the cavity shape after pulse electric discharge machining in Example of Embodiment 4.

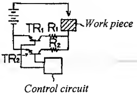
(Figure 1)



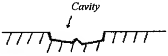
(Figure 2)



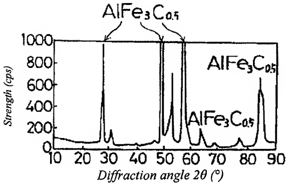
(Figure 5)



(Figure 15)



(Figure 3)



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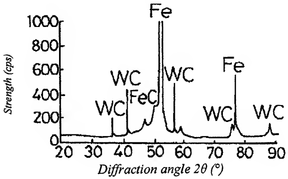
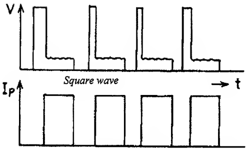
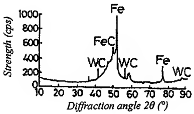


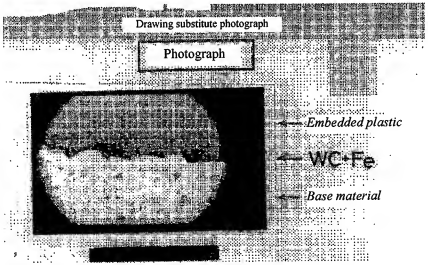
(Figure 6)



(Figure 7)



(Figure 8)



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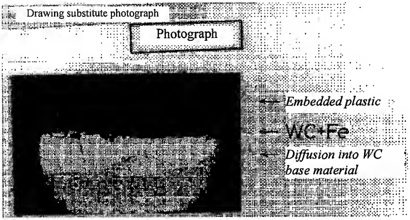
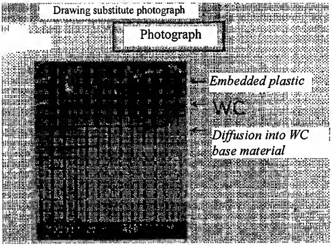
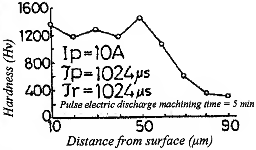


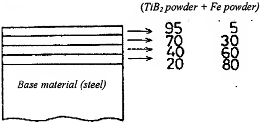
(Figure 10)



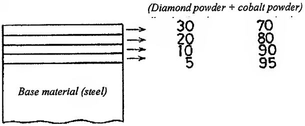
(Figure 11)



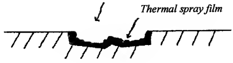
(Figure 12)



(Figure 13)



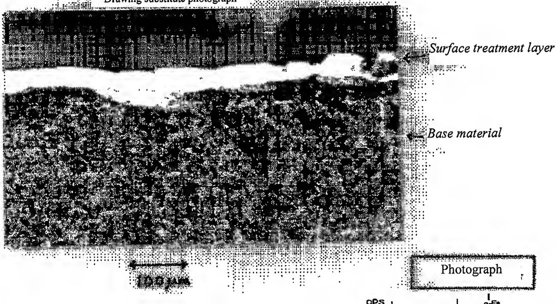
(Figure 14)



(AMENDMENT)
(Submission date) February 15, 1993
(Amendment 1)
(Document to be amended) Specification
(Item to be amended) 0042
(Method of amendment) Modification
(Content of amendment)
(0042) It should be noted that while electric discharge deposition or thermal spraying was used as the means of coating with the coating material in the above-described examples of embodiment, it is also possible to employ other means such as electrodeposition, low temperature vapor deposition, etc., and of course it is also possible to employ a combination of various coating means. Furthermore, it is of course also possible to repeat electric discharge deposition machining (primary machining) and electric discharge remelting machining (secondary machining) multiple times under the same or different conditions, an example of embodiment of which is presented below.
(Amendment 2)
(Document to be amended) Specification
(Item to be amended) 0043
(Method of amendment) Modification
(Content of amendment)
(0043)
(Example of Embodiment 5) In the present example, performing electric discharge deposition machining (primary machining) one time and electric discharge remelting machining (secondary machining) one time is counted as a single process, and multiple such processes are repeated in this example. This is effective when applied in cases where, if base material coating through electric discharge deposition machining (primary machining) and subsequent pulse electric discharge remelting machining (secondary machining) are performed just once, the surface layer would be partially blown off, leading to exposed portions of the base material surface, or where it would not be possible to form a thick surface treatment layer.
(Amendment 3)
(Document to be amended) Specification
(Item to be amended) 0044
(Method of amendment) Modification
(Content of amendment)
(0044) First, the machining parameters of the first pulse electric discharge deposition machining (primary machining) process were set to electrode material: powder electrode (same as the WC-Fe electrode used in Example of Embodiment 1), electrode polarity: negative, Ip: 25 A, τp: 8 μsec, τr: 512 μsec, machining time: 5 minutes, and the parameters of the second pulse electric discharge remelting machining (secondary machining) process were set to electrode material: copper plate, electrode polarity: negative, Ip: 15 A, τp: 1024 μs, τr: 1024 μs, machining time: 7 minutes. The other parameters were the same as in Example of Embodiment 1. Then, after forming a WC-Fe built-up alloy layer on the base material surface by electric discharge deposition in the same manner as in Example of Embodiment 1, the process of performing secondary machining was repeated 5 times. A cross-sectional photograph of the specimen using an optical microscope is shown in Figure 16, and X-ray diffraction analysis results are shown in Figure 17. Based on Figure 16, an approximately 50 μm thick built-up layer of uniform extent was confirmed. Furthermore, the presence of WC was confirmed based on Figure 17. The hardness of the specimen cross-section was measured to be approximately Hv 1650 on average, so a very high hardness was confirmed. Figure 18 is a cross-sectional photograph of a specimen using an optical microscope in the case where base material coating and pulse discharge remelting machining under the aforementioned secondary machining parameters were each performed once, showing a state where the surface treatment layer is discontinuous and not uniform. Figure 19 is the X-ray diffraction analysis results after primary machining.
(Amendment 4)
(Document to be amended) Specification
(Item to be amended) 0045
(Method of amendment) Addition
(Content of amendment)
(0045)
(EFFECT OF THE INVENTION) According to the present invention, as described in detail above, a compact strong coating layer having adequate thickness and the desired surface characteristics, such as corrosion resistance and heat resistance, can be easily formed without disadvantages such as dimensional change and reduction in hardness (strength) of the base material, or peeling of film, etc. For example, the invention can be employed for coating the parts of high temperature turbine blades that are bombarded by high temperature gases or steam, die cavity areas into which high temperature molten metal is cast, shot blasting nozzle parts for molten metal casting dies, and other parts (e.g. injection molding machine pipe parts, etc.), or for coating only the blade parts of steel dies, with fine ceramics.
(Amendment 5)
(Document to be amended) Specification
(Item to be amended) 0046
(Method of amendment) Addition
(Content of amendment)

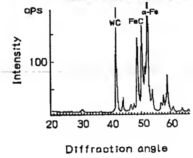
(0046) Furthermore, functionally graded materials having a so-called functionally graded film in which the composition changes gradually from the top of the base material toward the surface can be manufactured inexpensively.
(Amendment 6)
(Document to be amended) Specification
(Item to be amended) Figure 16
(Method of amendment) Addition
(Content of amendment)
(FIGURE 16) A micrograph (×160) of the cross-section of a specimen (metal structure) obtained by repeating electric discharge deposition (primary machining) and pulse electric discharge remelting machining (secondary machining) 5 times in Example of Embodiment 5.
(Amendment 7)
(Document to be amended) Specification
(Item to be amended) Figure 17
(Method of amendment) Addition
(Content of amendment)
(FIGURE 17) A drawing showing the X-ray diffraction results for the WC-Fe coating layer of a specimen obtained by repeating the primary machining and secondary machining processes in Example of Embodiment 5.
(Amendment 8)
(Document to be amended) Specification
(Item to be amended) Figure 18
(Method of amendment) Addition
(Content of amendment)
(Figure 18) A micrograph (×160) of the cross-section of a specimen (metal structure) obtained by repeating the primary machining and secondary machining process once in Example of Embodiment 5.
(Amendment 9)
(Document to be amended) Specification
(Item to be amended) Figure 19
(Method of amendment) Addition
(Content of amendment)
(FIGURE 19) A drawing showing the X-ray diffraction results for the specimen after primary machining in Example of Embodiment 5.
(Amendment 10)
(Document to be amended) Drawings
(Item to be amended) Figure 16
(Method of amendment) Addition
(Content of amendment)
(Figure 16)

Drawing substitute photograph



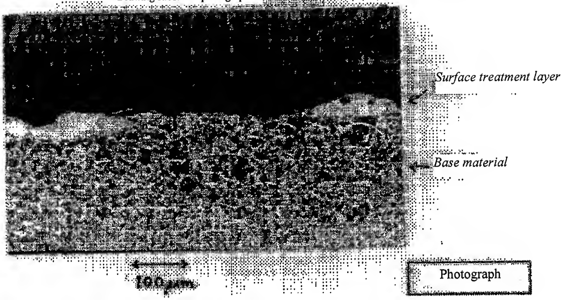
Photograph

(Amendment 11)
(Document to be amended) Drawings
(Item to be amended) Figure 17
(Method of amendment) Addition
(Content of amendment)
(Figure 17)



(Amendment 12)
(Document to be amended) Drawings
(Item to be amended) Figure 18
(Method of amendment) Addition
(Content of amendment)
(Figure 18)

Drawing substitute photograph



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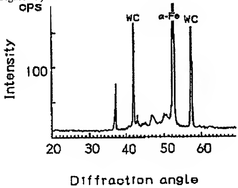
(Amendment 13)
(Document to be amended) Drawings
(Item to be amended) Figure 19
(Method of amendment) Addition
(Content of amendment)
(Figure 19)



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(51) Int. Cl.[5]	Identification codes	JPO file numbers	FI	Technical indications
C25D 5/50				